

CPMAS AND DDMAS ^{13}C NMR ANALYSIS OF COAL LIQUEFACTION RESIDUES

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INTRODUCTION

We have shown in previous papers that spectroscopic analyses of liquefaction residues (by NMR, pyrolysis-GC-MS, and FT-IR) can provide important structural information which can be used for elucidating the chemical reactions of liquefaction (Song et al., 1992, 1993, 1994) as well as the effects of dispersed catalysts (Saini et al., 1992; Huang et al., 1993; Song et al., 1994). The present work involves solid-state ^{13}C NMR studies of residues of two subbituminous coals from their liquefaction at 300–425°C, using cross-polarization (CP), dipolar dephasing (DD) and magic-angle-spinning (MAS) techniques. A preliminary survey of some CPMAS ^{13}C NMR results for one of the two coals was presented previously (Song et al., 1993). In a companion paper, we report on the analysis of oils from liquefaction of these coals by two-dimensional HPLC and GC-MS (Saini and Song, 1994).

EXPERIMENTAL

Sample Preparation. Three types of samples were examined in this study. The first set of samples are THF-insoluble residues from temperature-programmed liquefaction (TPL) of a Montana subbituminous coal (DECS-9) in tetralin solvent at a final temperature ranging from 300°C to 425°C for 30 min (Song et al., 1992). The second set of samples are THF-insoluble residues from liquefaction of a Wyodak subbituminous coal (DECS-8) at 350°C with and without a solvent (Song et al., 1994). The coals were predried in vacuum at about 100°C for 2 h prior to liquefaction. The third set of samples are the fresh raw coals (DECS-8, DECS-9) and THF-extracted but unreacted coals. Our experience shows that trace amounts of THF always remain in the THF-extracted residues even after vacuum drying at 100°C for over 6 h, which interferes with spectroscopic analysis. We have solved the problem by washing the residue first with acetone, then with pentane, followed by vacuum drying at 100°C for 6 h prior to spectroscopic analysis. The residue samples were also subjected to elemental analysis.

Solid-State ^{13}C NMR. NMR spectra were acquired on a Chemagnetics M-100 spectrometer. The measurements were carried out at a carbon frequency of 25.035 MHz. The spectrometer performance was checked with a standard sample of hexamethylbenzene to assure the Hartman-Hahn match. In a typical analysis, about 0.4–0.6 g of a sample was packed in a 0.4 mL bullet-type rotor made of polychlorotrifluoroethylene (Kel-F). Kel-F does not have a CPMAS ^{13}C signal. The MAS speed of the rotor was about 3.5 kHz.

The CPMAS ^{13}C NMR spectra were obtained by using the combined high power proton decoupling, cross-polarization, and magic angle spinning techniques. The experimental conditions for all the samples are as follows: a cross-polarization contact time of 1 msec, a pulse delay time of 1 sec, 50 kHz of proton decoupling, sweep width of 14 kHz, and 20–30 Hz line broadening. Carbon aromaticity was determined by integrating the peaks between 95 and 165 ppm (ppm relative to tetramethylsilane). Spinning sideband intensity was distributed for aromatic carbons. Other details concerning CPMAS maybe found elsewhere (Hatcher, 1987).

Dipolar-dephasing ^{13}C NMR spectra (DDMAS) were acquired by using the pulse sequence described by Alemany et al. (1983) and Wilson et al. (1984). After the protons are spin-locked and cross-polarization is induced, a variable dephasing time T_{dd} is inserted, during which the high-power decoupler is turned off. During this period, which lasts from 5 to 180 μsec , carbon magnetization becomes influenced and diminished (dephased) by the strong dipolar interactions between ^{13}C and ^1H spins. Carbons directly bonded to hydrogens (protonated carbons) dephase much more rapidly than those without attached hydrogens (non-protonated carbons). More details about the theory and procedures of dipolar dephasing may be found elsewhere (Hatcher, 1987, 1988; Pan and Maciel, 1993). In general, protonated carbons dephase within the first 60 μsec (T_{dd}), and the signals remain after 60 μsec are due to non-protonated carbons.

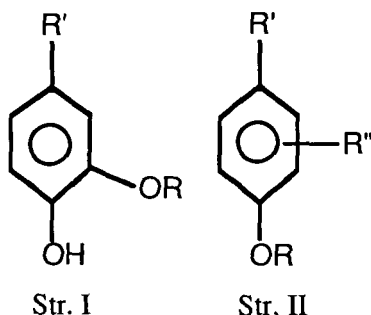
RESULTS AND DISCUSSION

Structural Characteristics of THF-extracted Coals

Figure 1 shows the CPMAS and DDMAS ^{13}C NMR spectra of THF-extracted but unreacted Montana subbituminous coal (DECS-9). In the CPMAS spectrum, there are two major bands, an aromatic bands from 95 to 165 ppm and an aliphatic band from 0 to 80 ppm. Among the aliphatic bands, methyl carbons appear at 0–25 ppm, methylene carbons resonate between 25–51 ppm, methoxyl groups around 51–67 ppm and ether groups between 67–93 ppm (Yoshida et al., 1987). The aromatic region includes two shoulders which may be attributed to catechol-like oxygen-bound carbons (centered around 142–144 ppm) and phenolic carbons (centered around 152–154 ppm). There are two other bands with lower intensities, including carboxyl groups between 170–190 ppm and ketonic carbonyl groups between 190–230 ppm.

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DDMAS ^{13}C NMR was used to examine the degree of protonation of carbons. Protonated carbons decay at a rate that is dependent on T_{dd}^2 and is often referred to as the Gaussian component of signal decay; non-protonated carbons decay at a much slower rate that is exponential with respect to T_{dd} (Alemany et al., 1983). Compared to the CPMAS spectrum, signal decay in the 95-165 ppm region was due mainly to protonated aromatic carbons (95-130 ppm). The signal intensity remaining in the aromatic region in the DDMAS spectrum in Figure 1 can be attributed to bridgehead and substituted aromatic carbons (130-148 ppm) and oxygen-bound aromatic carbons (140-165). Apparently, the shoulders that we identified as catecholic (structure I) and phenolic (structure II) carbons remain in the DDMAS structure and are clearly non-protonated carbons.



Our assignment of the peak centred at 142-144 ppm in the DDMAS spectra is different from that of Pan and Maciel (1993). They assigned the 144 ppm peak for Beulah-Zap lignite (801) to an aniline-type aromatic carbon. We have assigned this peak to the catecholic oxygen-bound aromatic carbon (shown in structure I). This is based on the NMR spectra of lignin-related model compounds and lignin (Hatcher, 1987) and the combined CPMAS NMR and pyrolysis-GC-MS studies of low-rank coals, including DECS-9 (Song et al., 1993) and DECS-8 (Saini et al., 1992) coals used in this work, as well as a lignite (Wenzel et al., 1993).

Flash pyrolysis GC-MS of lignites (Hatcher et al., 1988; Wenzel et al., 1993), DECS-9 Montana coal (Song et al., 1993), and DECS-8 Wyodak coal (Saini et al., 1992) revealed that catechol and phenol as well as their homologs are important components in the pyrolyzates of low-rank coals. Another important evidence is that as catechol observed in the pyrolysis-GC-MS diminishes, so does the catecholic peak in the CPMAS ^{13}C NMR spectra (Hatcher et al., 1988; Song et al., 1993; Wenzel et al., 1993).

Quantitative CPMAS NMR analysis of Montana coal was performed by means of curve-fitting, as described in our recent paper (Song et al., 1993). This coal has 63-64% aromatic carbons among total carbons. Combination of DDMAS and CPMAS NMR data reveals that about 34-35% of the aromatic carbons are protonated carbons; 23-24% of aromatic carbons are chemically bound to oxygen atoms; the remaining 31-33% aromatic carbons are bound primarily to other carbon atoms and secondarily to nitrogen and sulfur. The above spectroscopic results suggest that the Montana coal contains approximately two or three protonated carbons, one or two oxygen-bound carbons, and two substituted or bridgehead carbons per aromatic ring.

Compared to the Montana coal, THF-extracted Wyodak subbituminous coal (DECS-8) has a lower aromaticity (57%). However, it also has all the characteristic peaks (aliphatic, aromatic, carboxyl, carbonyl) and shoulders (phenolic, catecholic) that DECS-9 Montana coal possess (Figure 1). The DDMAS ^{13}C NMR data are not available for this sample at the present time.

Characterization of Residues from Non-Catalytic Liquefaction

Figure 2 presents the CPMAS and DDMAS ^{13}C NMR spectra of THF-insoluble residue from non-catalytic TPL of a Montana subbituminous coal (DECS-9) in the presence of tetralin solvent at a final temperature of 350°C for 30 min. Details of TPL procedures and results may be found elsewhere (Song and Schobert, 1992). Comparative examination of DDMAS data indicates at least three trends. First, relative to the THF-extracted unreacted coal, non-protonated carbons contribute more to the aromatic band in the residue from 350°C run. Second, the catecholic peak almost disappeared after 30 min at 350°C. Third, phenolic peak does not diminish as much as the catecholic peak upon reaction at 350°C, as can be seen by comparing the two DDMAS spectra (Figures 1 and 2).

Figure 3 shows the CPMAS and DDMAS ^{13}C NMR spectra of THF-insoluble residue from non-catalytic reaction of a vacuum-dried Wyodak subbituminous coal (DECS-8) in the absence of any solvent at 350°C for 30 min under 6.9 MPa H_2 . Since no donor solvent or catalyst was used, the coal conversion is very low, only about 12.5 wt%. More liquefaction results of this coal are described elsewhere (Song et al., 1994). The characteristics of both CPMAS and DDMAS spectra of this sample resemble those of the corresponding spectra for residue from Montana coal (Figure 2), although the two samples were derived from different coals under different conditions.

The reaction temperature has the most significant impact on the spectral characteristics of the liquefaction residues. We have performed both DDMAS and CPMAS ^{13}C NMR analysis of the THF-insoluble residues from TPL reactions of Montana coal (DECS-9) at 300, 350°C, 375, 400 and 425°C for 30 min. Catechol-like structures were found to be thermally sensitive and diminish gradually with increasing temperature up to 350°C. The catecholic shoulder at 142-144 ppm disappears from the residue of 375°C run. Carboxyl (165-190 ppm) and carbonyl (190-230) peaks diminish significantly after 375°C and they disappear in the spectrum of residue from 400°C run. Phenolic structures diminish with increasing temperature up to 425°C. These results clearly indicate that there are thermally reactive oxygen functional groups in coal and their reactions can take place at temperatures as low as 300-375°C.

As shown in Figure 4, the carbon aromaticity of residues increased monotonically with increasing reaction temperature after 300°C. Comparison of the curve for H/C atomic ratio and that for carbon aromaticity

indicates that THF extraction of unreacted coal and that reacted at 300°C, removed more aliphatic materials. However, the conversion level at 300°C in tetralin is below 10 wt% (dmmf). The H/C ratio of the residues decreased significantly with increasing temperature up to 425°C. The aromaticity of the residues increased with increasing coal conversion, being consistent with the observations by two other groups on residues from liquefaction (Fatemi-Badi et al., 1991; Franco et al., 1991). The increase in carbon aromaticity is driven primarily by temperature, and secondarily by the adduction of aromatic solvent molecules (Song et al., 1993, 1994). Another interesting observation is that, while the total aliphatic carbons decrease, the percentage methyl carbons relative to total aliphatic carbons increases with increasing temperature up to 425°C.

DDMAS analysis (Figure 5) shows that the degree of protonation of aromatic carbons in the residues decreased from 35% (for THF-extracted but unreacted Montana coal) to 13% for residue from the non-catalytic run at final reaction temperature of 375°C. General trends observed from DDMAS experiments for residues from DECS-9 are as follows. The degree of protonation of aromatic carbons in the residue decreases with increasing coal conversion. In other words, the higher the coal conversion into THF-soluble products, the more non-protonated aromatic carbons in the THF-insoluble residues. The higher content of non-protonated carbons among total aromatic carbons could originate from either higher degree of condensation or higher extent of substitution. Since the aromaticity increases and atomic H/C ratio decreases with increasing temperature, the decrease in the relative content of protonated aromatic carbon (or the increase of non-protonated aromatic carbons) is due mainly to the increased degree of condensation. This means that there are more bridgehead aromatic carbons or more condensed-ring aromatic structures in the residues from runs at higher temperatures.

As discussed above, there exists good correlation between carbon distribution and reaction temperature above 300°C. We have attempted mathematical correlation of the NMR data for the residue with reaction temperature (Song et al., 1993). Figure 6 shows that the changes in the aromatic, aliphatic, and oxygen-bound carbons of the residues can be related to the liquefaction temperature by a linear correlation. A general expression is given below:

$$C_i = \alpha f_i + \beta T \quad \text{for specific carbon type } i \quad (1)$$

where T is reaction temperature (°C), f_i and C_i represent the content of specific carbons (%) in the original coal and residue, respectively, and α and β are constants. The specific correlations for aromatic C (C_{ar}), aliphatic C (C_{alip}), and oxygen-bound carbons (C_{O-C}) are given in Figure 6. We have quantitatively analyzed the NMR spectra of 26 residues from liquefaction of DECS-9 coal under various conditions with and without solvents (Song et al., 1993). The results show that equation 1 holds for all the cases with good linear correlation.

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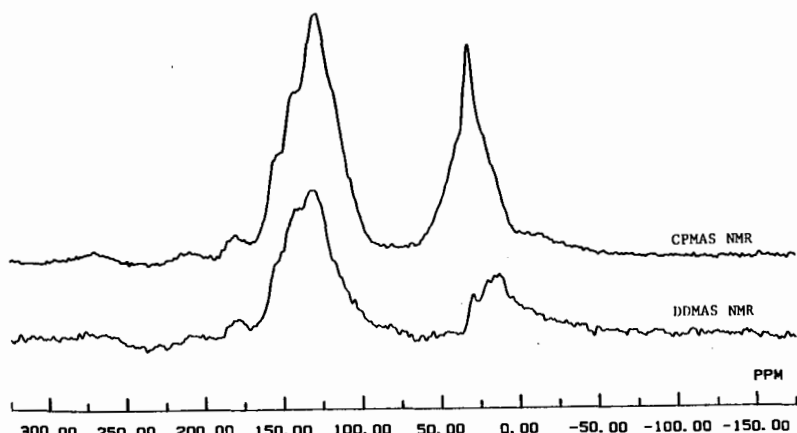


Figure 1. CPMAS and DDMA5 ^{13}C NMR spectra of THF-extracted but unreacted Montana subbituminous coal (DECS-9). For DDMA5, Tdd = 60 μs .

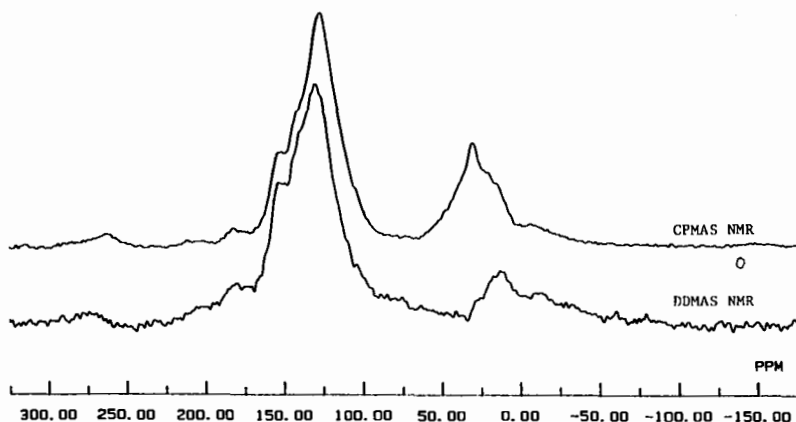


Figure 2. CPMAS and DDMA5 ^{13}C NMR spectra of residue from TPL of Montana coal in the presence of tetralin at a final temperature of 350°C for 30 min. For DDMA5, Tdd = 60 μs .

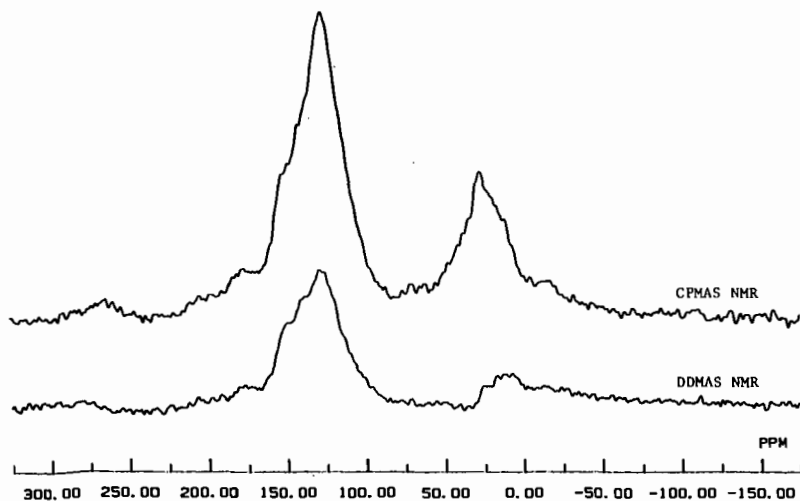


Figure 3. CPMAS and DDMA5 ^{13}C NMR spectra of residue from liquefaction of Wyodak coal (DECS-8, vacuum-dried) without any solvent at 350°C for 30 min. For DDMA5, Tdd = 60 μs .

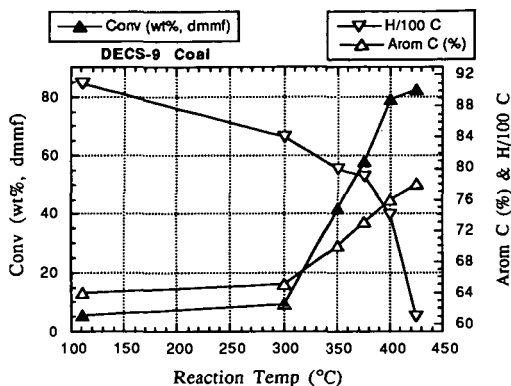


Figure 4. Conversion of Montana coal and changes in aromaticity (Arom C, %) and No. of H atoms/100 C in the residues versus final temperature of liquefaction (TPL) in tetralin.

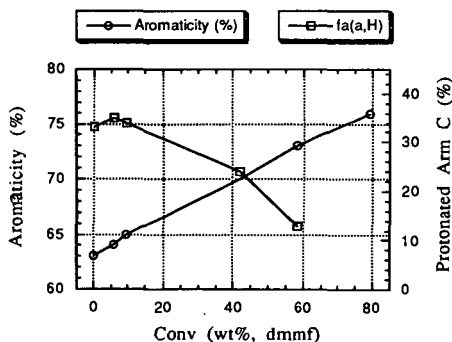


Figure 5. Change of aromaticity and percentage degree of protonation of aromatic carbons [fa(a,H)] in the residues versus conversion of DECS-9 Montana coal in TPL with tetralin.

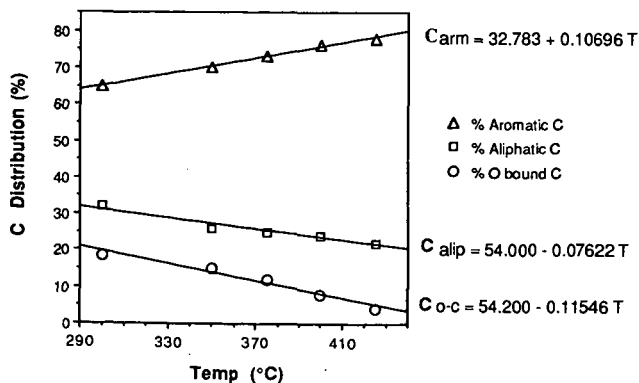


Figure 6. Linear correlation of contents of aromatic, aliphatic, and total oxygen-bound carbons in residues from DECS-9 Montana coal with final temperature of TPL in tetralin.